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Oxidized Cellulose

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IT HAS BEEN A MATTER of common observation for a long time that cellulose, whether in the form of paper or cloth, on long exposure to atmospheric conditions undergoes certain changes which cause a notable decrease in fiber strength. The cotton textile industry had been familiar for many years with the phenomenon of "tendering" which occurs in cotton fabrics when they are bleached in relatively strong solutions. This was manifest chiefly in the loss of fiber strength and an inability to accept certain dyes in the same manner as unmodified cotton.

Witz (*1*, *2*) was the first to study this modified cotton. He found that cotton which had been treated with a hypochlorite bleach possessed a lower carbon content, and a correspondingly higher oxygen content, than that which had not been so treated. An oxidative process was suggested, and consequently the term "oxycellulose" was coined to describe the modified cellulose. This choice of nomenclature was unfortunate, for it tended to create the impression that the products were homogeneous in nature, and obscured the fact that apparently a variety of complex products is formed which cannot be described collectively under any such rigid term as "oxycellulose." This nomenclature persisted for many years, but recently the term "oxidized cellulose" has been in more general use in the literature.

The "oxycellulose" of Witz consisted of a white, dusty powder resembling starch. When treated with dilute alkaline solutions, a small portion of it dissolved, and the insoluble portion was termed "alpha-oxycellulose." Witz was interested from a technical standpoint in the ability of oxycellulose to absorb basic dyes without the use of mordants. From the results which he obtained, however, Cross and Bevan (*3*) concluded that cellulose has a relatively stable carbon nucleus, with functional groups capable of being attacked by oxidizing agents. They speculated on the presence of alcoholic hydroxyl groups, since the oxidized product displayed the properties of an aldehyde, and, to a certain measure, those of an acid.

Formation

These early investigations gave a great impetus to the study of the effect of oxidizing agents upon cellulose. Subsequent investigators treated cellulose with a wide variety of oxidants under various conditions. They obtained products whose physical appearance was similar; namely, friable powders or, at best, short fibers of microscopic size. Some of the oxidizing agents used at various pH values and reaction temperatures were hypohalite solutions, nitric acid, per-

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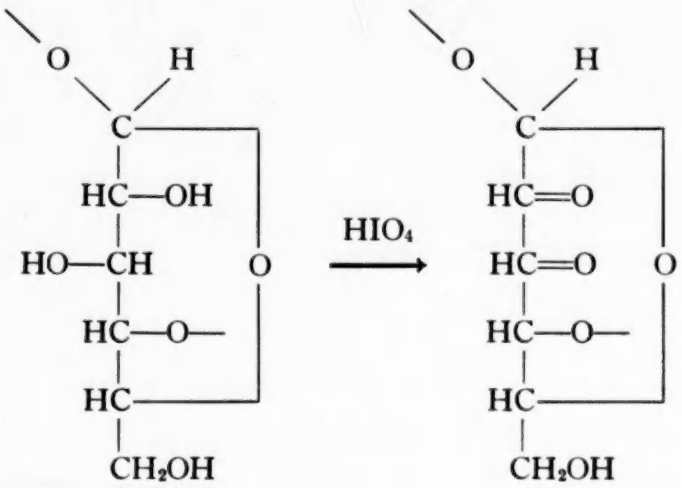
manganate solutions, hydrogen peroxide, dichromate solutions, ozone, persulfate solutions, and even oxygen generated electrolytically in a conducting solution. Gradually two general types of oxidized cellulose came to be recognized, the "methylene blue" type and the "reducing" type. The former was characterized by a high methylene-blue absorption, a low copper number, and a low alkali solubility, whereas the latter possessed a low methylene-blue absorption, a high reducing value, and a comparatively high alkali solubility.

The hydrolytic action of these oxidizing solutions was not appreciated at first, but was realized later when the chemical structure of cellulose was elucidated. The oxidation was accompanied by a concomitant rupture of the hemiacetal linkages of the cellulose, resulting in a shorter chain length, as evidenced by the degraded fiber structure. When conditions were chosen to obtain a minimum of fiber degradation, it was found that relatively little oxidation took place. Elementary analyses for carbon and hydrogen contents indicated in general that under the most favorable conditions the degree of oxidation was low. Furthermore, acid hydrolysis of the products made it possible to obtain large quantities of glucose, showing that the major portion of the cellulose chain was unattacked by the oxidant.

Structure

For many years there was little of importance contributed to the knowledge of the fundamental chemical structure of oxidized cellulose. Renewed impetus was given to its study by the discovery, in 1937, of two new oxidizing agents—periodic acid and nitrogen tetroxide. These appear to yield homogeneous products, a fact which facilitates their structural investigation. Jackson and Hudson (*4*) showed that simple sugars and sugar derivatives are selectively oxidized by periodic acid at the second and third carbon atoms of the monosaccharide units. On the assumption that the same reaction mechanism would apply to cellulose, they predicted that periodic acid would oxidize the anhydroglucose units of the cellulose at the second and third carbon atoms, as follows (*5*):



Hydrolysis of such a product, and subsequent mild oxidation, should give as the principal products *d*-erythronic acid and oxalic acid. This was found to be the case. In these experiments the cellulose was oxidized with ½ molar periodic acid solution at room temperature to yield a product which retained a fibrous structure, though considerable shrinkage occurred. The oxidation was rapid in the early stages but gradually decreased, and stopped when approximately one mole of oxygen was consumed for each anhydroglucose unit. Thus, for the first time in over 50 years, a well-defined, highly oxidized cellulose was obtained by means of a known mechanism.

In 1942, Yackel and Kenyon (*6*) published the results of an investigation of the effect of nitrogen tetroxide on cellulose. The fibrous material obtained contained no nitrogen, but was entirely different chemically from the original cotton. Physically the material appeared unchanged. Its most notable property was rapid and complete solubility in dilute alkaline solutions.

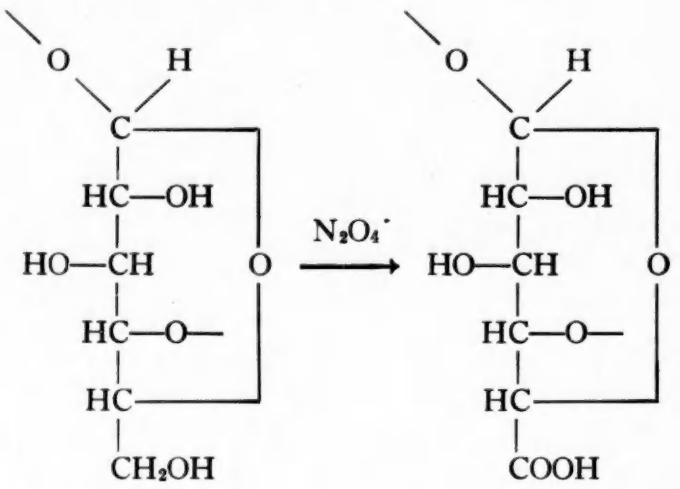
In this case the cotton fibers were subjected to the vapors of dry nitrogen tetroxide in an all-glass vessel. Oxidation was rapid at first but showed a marked decrease in velocity within a few hours.

The optimum reaction temperature was found to be slightly above the boiling point of the nitrogen tetroxide (21.6°C.). The fibrous product was washed free of acid with distilled water and air-dried at room temperature.

The very ready solubility of the material in dilute alkali indicated the presence of carboxyl groups. This solubility was evident also in dilute sodium bicarbonate solution and even in aqueous pyridine. This in turn suggested that the sixth carbon in the anhydroglucose residue had been attacked. Analyses of the product gave results whose highest values, even after prolonged oxidation, did not exceed one carboxyl group per C_6 unit. If the sixth carbon were to be selectively oxidized to a carboxyl group, the result would be a polyuronic acid which, on boiling with dilute hydrochloric acid, should quantitatively produce CO_2. This was found to be the case, and analysis by alkaline titration was found to check closely with the CO_2 evolution. At the same time, furfuraldehyde should also be produced and can be isolated in the form of a phloroglucide or a phenylhydrazone. The yield is not quantitative by any means, but a considerable portion of it can be accounted for. This seemed to indicate that there was little change in the rest of the molecule.

Additional evidence of the structure of this material was obtained by Unruh and Kenyon (*7*) through acetylation of the oxidized celluloses. The resulting acetates were analyzed, and their acetyl contents were found to approximate closely the calculated values. This calculation was based on the assumption that the carbon dioxide evolution represented an equivalent quantity of combined uronic acid that was capable of yielding a diacetate. The remainder was taken to represent unattached anhydroglucose units that formed a normal triacetate. Such agreement of results would not be possible if oxidation had taken place to any great extent other than at the sixth carbon of the glucose unit.

This type of oxidation is thus quite selective, although the reaction mechanism itself is different from that encountered in the periodic acid oxidation. The nitrogen tetroxide mechanism may be represented as follows:



Considerable research has also been conducted by Davidson (*8*) on the physical properties of oxidized celluloses, especially the relation between viscosity and chain length. As yet there has been no satisfactory explanation for the decreased viscosity of an oxidized cellulose dissolved in alkali. Davidson has a plausible explanation for this observation in that groups near the hemi-acetal linkages are affected during the oxidation in such a manner as to weaken the resistance of these linkages to alkali, with a resulting shortening of the chain lengths.

Literature Cited

(*1*) Witz,O., *Bull. Soc. Ind.*,Rouen, *11*, 228 (1883).

(*2*) Clifford, P. H., and Fargher, R. G., *J. Textile Inst.*, *13*, 189 (Transactions) (1922).

(*3*) Cross, C. F., and Bevan, E. J., *J. Chem. Soc.*, *43*, 22 (1883).

(*4*) Jackson, E. L., and Hudson, C. S., *J. Amer. Chem. Soc.*, *59*, 2049 (1937).

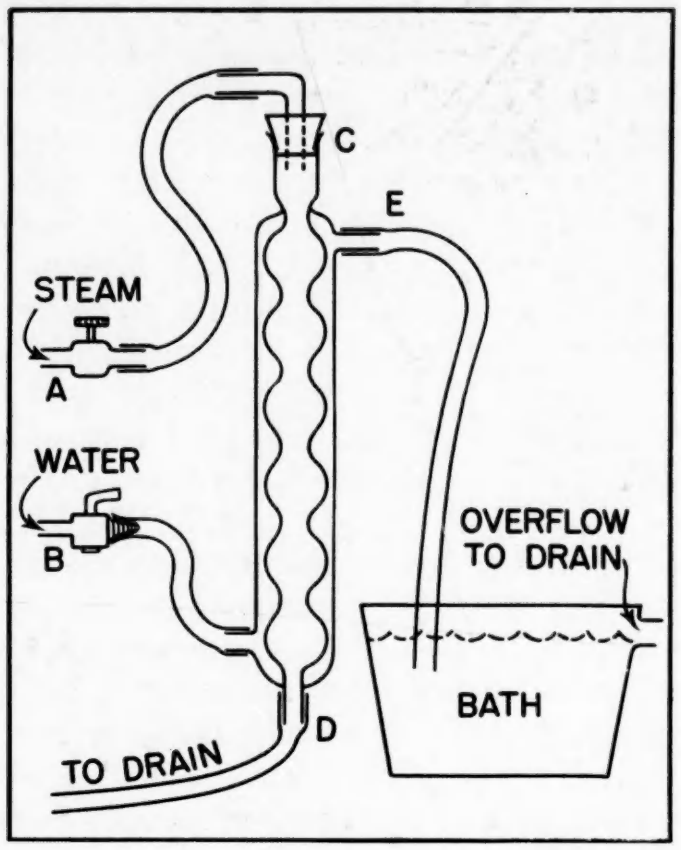
(*5*) Jackson, E. L., and Hudson, C. S., *J. Amer. Chem. Soc.*, *60*, 989 (1938).

(*6*) Yackel, E. C., and Kenyon, W. O., *J. Amer. Chem. Soc.*, *64*, 121 (1942).

(*7*) Unruh, C. C., and Kenyon, W. O., *J. Amer. Chem. Soc.*, *64*, 127 (1942).

(*8*) Davidson, G. F., *J. Soc. Dyers & Colourists*, *56*, 58 (1940); *J. Textile Inst.*, *31*, T81-96 (1940); *ibid.*, *32*, T109-31 (1941); *ibid.*, *32*, T132-48 (1941).

A Constant-Temperature Bath



MOST TYPES of constant-temperature bath apparatus are complicated and difficult to assemble. The sketch reproduced at the right, however, illustrates a constant-temperature bath for temporary use which has the advantages of simplicity and availability of materials, plus rapidity and ease of assembly and adjustment. This apparatus is composed of materials commonly found in most laboratories, and will maintain a temperature constant to within about 1°C. over a period of several days.

Although the ordinary steam valves used in the laboratory permit considerable fluctuation in the flow of steam, the usual type of petcock used for water is capable of a fairly fine adjustment and permits a substantially constant flow over considerable periods of time. In the apparatus illustrated, an excess of steam is run from the steam valve (A) into the top (C) of the condenser, which is set up as a heat interchanger. At the same time a closely adjusted stream of water from the petcock (B) is circulated through the condenser, emerging at (E). The excess steam, together with the hot condensate, escapes at (D) and may be run directly to the drain; or it may be run through a second condenser having a separate cooling system, in order to keep the steam out of the air. The constant-temperature water emerging from (E) may be run to a vessel with an overflow to serve as a bath, as shown in the sketch; or, if it is desired to use this warm water in the jacket of a condenser or for some similar purpose, it may be used directly without any necessity for a circulating pump. It is well to check the temperature occasionally, say once a day, and, if necessary, to adjust the flow of tap water to compensate minor variations in the water temperature.

An ordinary glass-bulb condenser, as shown in the sketch, is quite suitable for maintaining temperatures in the range of about 40°–70°C. If temperatures much lower than this range are desired, a smaller or less efficient condenser would be preferable; for much higher temperatures, or for a greater volume of water, a larger or a more efficient condenser, such as one built of metal, would be required. With any given condenser, the temperature of the bath is inversely dependent upon the rate of flow of the water. An excess of steam emerging from the heat interchanger is essential at all times; otherwise, the temperature will fluctuate to some extent, depending upon the amount of steam present.

This type of constant-temperature bath is quite useful when it is desired to heat individual reactions to different temperatures. It also facilitates operations in which it is desired to heat and maintain a reaction mixture at a definite temperature, followed by cooling for a time, since by merely turning off the steam the warm water quickly becomes cold and thus serves as a cooling bath.

This apparatus is not recommended when extreme accuracy is required nor when it is desired to maintain a bath over long periods of time.